

PATENT SPECIFICATION

1,004,272

1,004,272



Date of Application and filing Complete
Specification: April 3, 1963.

No. 13161/63.

Application made in United States of America (No. 186335) on
April 10, 1962.

Complete Specification Published: September 15, 1965.

© Crown Copyright 1965.

Index at Acceptance:—C3 P (2D1A, 2D1B, 2D2A, 2K7, 2K8, 2T2E).

Int. Cl.:—C 08 d.

COMPLETE SPECIFICATION

NO DRAWINGS

Vulcanizable Composition and Vulcanizing Process.

WE, MORTON SALT COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 110 North Wacker Drive, Chicago, Illinois, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved processes for vulcanizing and curing of elastomeric materials utilizing novel adducts of magnesia and organic vulcanizing agents and to improved vulcanizable elastomer compositions incorporating these adducts.

It is conventional in the processing of rubber goods, including natural and synthetic rubbers and elastomers, to use a vulcanizing agent to carry out the curing step. Most common of the rubber vulcanizing agents is sulfur, which is ordinarily used in conjunction with a vulcanizing accelerator. The use of an accelerator substantially shortens the vulcanization process. While sulfur is a vulcanization agent that is essentially inorganic in character, the accelerators, which are vulcanization agents of themselves, are organic compounds.

One of the difficulties has been that while a particular accelerator may enhance the rate of cure and substantially reduce the curing time, it may also produce complications in the form of premature vulcanization commonly known as scorch. Careful selection of accelerators and accelerator systems in a particular vulcanization process was necessary to provide the required safety. The highly active nature of some accelerators led to their discard by the industry because of inability to control premature vulcanization or scorch. This difficulty of scorch is, in part, a result of the nature of the rubber compounding

process.

Vulcanizing agents, such as accelerators, are present in vulcanizing rubber stocks in relatively small amounts. In order to obtain uniformity in the final cured product it is necessary to mix the rubber stock thoroughly to disperse the accelerator throughout the mixture to eliminate localized defects caused by different rates of cure. It is well known that very small amounts of material are difficult to disperse throughout a larger mass. Inherent in the dispersion procedures used by the rubber industry are processing techniques which involve the use of high shear blending equipment, usually supplemented with heat to improve flowability and plasticity during the mixing and handling steps. These high shear mixing processes, both with and without added heat, produce localized high temperatures which in turn produce premature activation of the accelerator, and result in scorch of the rubber stock.

Accordingly it would be desirable to provide a vulcanization agent for elastomer stocks which would be in such a form as to represent a larger weight percentage of the total compounding ingredients and permit more rapid dispersal in the rubber or elastomer mix. The introduction of the accelerator or vulcanizing agent in the form of a mechanical mixture with a diluent material would obviously not accomplish this result since the diluent merely adds to the sum total of solids throughout which the organic vulcanization agent must be dispersed.

Since many of the known organic vulcanizing agents have many desirable attributes, aside from a tendency to scorch, it would be desirable to modify these known materials in such a manner as would control scorching during the mixture and blending operations involved in the preparation of vulcanizing stocks, but permit

[Price 4s. 6d.]

full use of vulcanization enhancement properties under vulcanizing conditions.

It has been found that conventional organic vulcanizing agents may be substantially modified to eliminate many of the problems which have heretofore been associated with their use by forming an adduct of these organic vulcanizing agents with a lightly calcined magnesia, such as disclosed in patent application Serial No. 13162/63 (Serial 1002207).

More particularly, the present invention provides a process of vulcanizing elastomeric material by incorporating into an elastomeric vulcanizable stock an adduct of an organic vulcanizing agent and a lightly calcined magnesia having an iodine adsorption number of from 10 to 300, and heating the resulting composition at vulcanizing temperatures to cure the elastomeric material.

The improved vulcanization process of this invention provides increased process safety without significant sacrifice of vulcanization speed and results in improved physical properties in the final product.

This invention also provides a vulcanizable elastomeric composition comprising an unvulcanized rubbery elastomer and an adduct of an organic vulcanizing agent and a lightly calcined magnesia having an iodine adsorption of from 10 to 300.

The organic vulcanizing agents are well known compositions and are preferably those which contain up to 20 carbon atoms. Particularly preferred vulcanizing agents for use as adducts with magnesia in this invention are those selected from the group consisting of amines, substituted aryl amines, aldehyde amines, guanidines, pyrimidines, thiazoles, thiocarbamates, thiuram sulfides, thioureas, imidazoles, polyhydroxy benzenes and mixtures thereof.

Exemplary of said amine type vulcanizing agents are aniline, p-phenylenediamine, p-aminodimethylaniline, p-nitrosodimethylaniline, o-m- and p-hydroxyaminobenzenes. "Aldehyde-amines" as a group includes condensation products of aldehydes and amines, such as hexamethylenetetramine, triethylenetetramine and 1,3,5-triethylhexahydro-s-triazine (sold as "Trimene Base"—"Trimene" is a registered Trade Mark).

Guanidines may be exemplified by guanidine, diphenyl-guanidine (DPG) and di-o-tolylguanidine (DOTG). Thioureas may be exemplified by trimethylthiourea (THIATE E), N-ethyl-N'-N'-dimethylthiourea (Thiate B), thiocarbanilide (N,N'-diphenylthiourea) and pyrimidines by thiohydropyrimidine. Thiazoles may be exemplified by mercaptobenzothiazole (MBT), N-cyclohexyl-2-benzothiazyl sulfenamide ("Santocure"—a registered Trade Mark), di(2-benzothiazylthiomethyl)-urea (El Sixty),

2-mercaptothiazoline (MT), and mercaptobenzothiazole disulfide (MBTS). 2-Benzothiazyl-N,N-diethylthiocarbamyl sulfide may be considered as exemplary of a thiocarbamate and thiazole derivative. Thiuram-sulfides may be exemplified by dipentamethylenethiuram di-sulfides and tetramethylthiuram monosulfide. Imidazoles may be exemplified by 2-mercaptoimidazoline (NA-22). Polyhydroxybenzenes may be exemplified by catechol, resorcinol, phloroglucinol, and hydroquinone.

While the foregoing are exemplary of many elastomer vulcanization agents, it should be understood that other materials falling within the above description may also be used in preparing these adducts.

The adducts of magnesia and the vulcanizing agent are formed by contacting a magnesia having an iodine adsorption number of from 10 to 300 or preferably from 15 to 220. The iodine adsorption of magnesia or magnesium oxide refers to the milligrams of iodine adsorbed per gram of dry magnesium oxide. The procedure for determining the iodine adsorption as that term is used herein is defined in patent application Serial No. 13162/63 (Serial 1002207).

The adducts are formed as indicated by containing the lightly calcined magnesia with an organic vulcanizing agent. The temperatures used in this reaction vary but broadly extend from 0 to 225°C., and preferably from 65 to 170°C. The contacting may be carried out by admixing the reactant in a solvent media, preferably an inert solvent, such as benzene, toluene, xylene, heptane, carbon tetrachloride or the like. Low polarity solvents are preferred. The contacting may also be carried out in the absence of solvent media, such as in those instances where the organic vulcanizing agent is a liquid material and an excess of this reactant may be used as the reaction media. Likewise the formation of these adducts may be carried out by fluid bed techniques whereby an organic vulcanizing agent is vapourized and passed through a bed of finely divided pulverulent magnesia of the type previously defined under fluidizing conditions, all as is more completely described in my aforesaid copending applications.

The "wet batch" and fluid bed technique described above are preferably carried out under essentially anhydrous conditions.

Certain magnesium oxide adducts may also be prepared by the use of two or more organic vulcanizing agents to produce a product having a balance of vulcanizing properties which are not obtainable by the expedient of simple admixing of the two organic materials.

The magnesia adducts described in the

foregoing are products which differ in vulcanizing properties substantially from a mixture of magnesium oxide and the organic material. The modifications result in a product which is much more versatile in the vulcanization process and in many instances overcomes drawbacks which the industry considered sufficient to militate against the use of the organic product in many vulcanization stocks.

It is intended that organic accelerators be included within the term "organic vulcanizing agent" as used herein. These organic accelerators may, depending upon the elastomer being cured, be used as the sole curing agent for an elastomer. 2-Mercaptoimidazole (NA-22) is exemplary of such a composition used in neoprene stock. Accordingly it is contemplated that the improvements of this invention may be carried out by the addition of the magnesia adducts of the organic vulcanizing agent to conventional elastomer stocks containing sulfur, anti-oxidants, fillers and reinforcing agents, plasticizers and the like. The organic vulcanizing agent adduct with magnesia is usually incorporated at levels which with respect to the organic portion of adduct, are comparable to those used in conventional compounding stocks. Accordingly the adduct may, in one specific aspect of the herein described process, be incorporated into the rubber curing stocks in amounts whereby the organic component constitutes from 0.05 to about 10 percent and preferably from about 0.5 to 5.0 percent by weight of the elastomer.

Generally the magnesia adduct utilized in the process of the present invention may contain from 1 to 35 percent organic vulcanizing agent, and preferably from about 2.5 to 15 percent organic vulcanizing agent.

The vulcanizing stocks include vulcanizable rubbery elastomers in general, such as for example natural rubber, synthetic rubbers, such as polychloroprene, butadienestyrene rubber (SBR), acrylonitrile-butadiene rubber, such as NBR, butyl rubber, polyacrylate rubber, such as butylacrylate rubber "Hycar" 4021 or Lactoprene EV—"Hycar" is a registered Trade Mark) poly-sulfide rubbers, such as "Thiokol" (registered Trade Mark), silicone rubbers, chloro-sulfonated polyethylene rubber, such as "Hypalon" (registered Trade Mark); fluoro elastomers (KX-2141), polyester elastomers, so-called synthetic "natural" rubbers and reclaimed rubber.

The type of vulcanization stocks which may be cured by the use of organically modified magnesias may contain anti-oxidants, antiozonants, plasticizers, resins, fillers, such as carbon black, fatty acids, zinc oxide, inorganic vulcanizing or curing agents, such as sulfur, metal salts, or the

like. The vulcanizing stocks may contain additional organic vulcanizing agents, such as an accelerator in a free or modified form, additional unmodified magnesia, and other organically modified magnesias.

For a more complete understanding of the improved process and compositions of this invention, reference is made to the following examples:

Example I

Polychloroprene vulcanization

A polychloroprene vulcanizing stock having the following formula was prepared:

Polychloroprene (Neoprene W)*	100	parts	80
Zinc oxide	5.0	parts	
Stearic acid	0.5	part	
Stabilizer ("Agerite Stalite S")**	2.0	parts	
Plasticizer (Circo light oil)	5.0	parts	85
Thermal Carbon black ("Thermax"—registered Trade Mark)**	75.0	parts	
Vulcanizing Agent (see A and B following)	9.3	parts	

The vulcanizing agent A and B, respectively, was incorporated into the foregoing formulation and the corresponding rubber stocks identified as A and B respectively. Mooney Scorch tests (ASTM D-1646-61) were run on each of the stocks to ascertain changes in process safety. The vulcanization agents used, A and B, were as follows:

Vulcanization Agent

- A: A physical mixture of 8.55 parts of magnesia, iodine No. 100, and 0.75 parts Thiato B (N-ethyl, N',N'-dimethyl thiourea);
- B: The reaction product of 8.55 parts magnesia, iodine No. 100, and 0.75 parts Thiato B, *supra*

Stock Containing:

Mooney Scorch Time (Minutes)

5 point rise 10 point rise

Vulcanization Agent A	27	34
Vulcanization Agent B	44	60

From the above it may be observed that Mooney Scorch time is considerably increased by the use of adduct of magnesia and an organic vulcanizing agent as compared with the physical mixture. Accordingly, the higher Mooney Scorch values indicate that a longer period of processing of elastomer stock is possible, without premature vulcanization, with vulcanization agent B. The stocks, when vulcanized, had comparable physical properties.

The following examples will illustrate the improved physical properties obtained in the use of adducts of magnesia and organic vulcanizing agents, accelerators, etc., as compared to comparable mixtures of the components in the same proportions in the

- vulcanizing stock of Example 1. The Mooney Scorch times are indicated under the respective headings, i.e. "mixture" and "adduct". The vulcanizing stock had the following composition :
- | | | | |
|-------------------------|-----------|---|-------------|
| Neoprene W | 100 parts | naphthylamine) | 2 parts |
| Stearic Acid | 1 part | Carbon black (SRF) | 29 parts 10 |
| Neazone A (phenyl-alpha | | Zinc oxide | 5 parts |
| | | Accelerator-magnesia : | |
| | | (as indicated in Table II) | |
| | | Examples 3, 5, 6, 7 and 8 include two organic accelerators in both the mixture and the adduct : | 15 |

TABLE II

Components of Magnesia-Accelerator Mixtures and Adducts				Mooney Scorch Time (6)			
				Minutes to a 10 point rise		% Organic	
Example	Accelerator Compound	Parts(7)	Magnesia Parts(5) (7)	Mixture	Adduct	Adduct and Mix	
20	2	Catechol	0.53	4.0(4)	9	14	11.94
25	3	Catechol	0.40	4.0	16	23	11.43
		DOTG(1)	0.12				
	4	Resorcinol	0.62	4.0	19	43	13.55
	5	Resorcinol	0.39	4.0	36	47	12.51
30		DOTG(1)	0.18				
	6	Resorcinol	0.39	4.0	25	39	13.07
		TETA(2)	0.21				
	7	Resorcinol	0.39	4.0	25	55	12.68
35		Trimine Base(3)	0.27				
	8	Phloroglucinol	0.56	4.0	37	75	12.68
		DOTG(1)	0.13				
	9	o-amino-phenol	0.354	4.0	31	42	8.12
40	(1)	DOTG : di-o-tolylguanidine					
	(2)	TETA : triethylenetetramine					
	(3)	Trimene base : 2,4,6-triethylhexahydro-s-triazine					
	(4)	Adduct contained 4.3 parts magnesia					
	(5)	Iodine No. 170					
45	(6)	Small rotor Mooney Scorch tests, 250°F. (ASTM-D-1646-61)					
	(7)	By weight					
Example 10				(1) American Cyanamide 2,2'-methylene-bis (4-methyl-6-t butyl phenol)			
As a further example, an adduct of 0.63 part ethylene thiourea (2-mercaptoimidazoline) and 5 parts of magnesia (iodine adsorption number of 20) prepared by the procedure set forth in application Serial No. 13162/63 ((Serial 1002207), was incorporated into a chlorobutyl rubber vulcanization stock (C). A control formation (D) was prepared using a mixture of the components in the adduct, in the same proportions.				(2) Iodine adsorption No. 200			
				(3) 0.63 part ethylene thiourea and 5.0 parts magnesium oxide — iodine No. 20			
				(4) By weight			
				(5) The rubber stocks identified as "C" and "D" above were cured for 60 minutes at 320°F. They had the following physical properties :			
				C			
				D			
				Tesile strength (psi)			
				2050			
				1740			
				Elongation			
				293			
				247			
				Tensile product*			
				6.0			
				4.3			
				*Product of tensile strength and elongation × 10 ⁻⁵ .			
				The improved tensile properties of Stock C as compared to Stock D are readily apparent.			
				While the foregoing examples are specific to certain vulcanizing agents or adducts, it should be understood that many other accelerators-curing aids may be used for this purpose.			
FORMULATION							
Chlorobutyl rubber (Enjay MD-551)							
Antioxidant							
"2246"(1)							
Carbon black (furnace black)							
Magnesia (2)							
Ethylene							
Thiourea							
Adduct(3)							

The improved tensile properties of Stock C as compared to Stock D are readily apparent.

While the foregoing examples are specific to certain vulcanizing agents or adducts, it should be understood that many other accelerators-curing aids may be used for this purpose.

In certain instances additional benefits are obtained in the way of improved compression set, tensile, volume swell and bin aging characteristics.

5 WHAT WE CLAIM IS :—

1. The process of vulcanizing elastomeric materials which comprises incorporating in an elastomeric stock an adduct of an organic vulcanizing agent containing up to 20 carbon atoms and a lightly calcined magnesia having an iodine adsorption number of from 10 to 300 and heating at vulcanizing temperatures to cure the elastomeric material.
- 15 2. The process according to claim 1 wherein the organic vulcanizing agent of said adduct is selected from amines, aldehyde - amines, guanidines, pyrimidines, thioureas, thiazoles, thiocarbamates, thiuram sulfides, imidazoles, polyhydroxy benzenes or mixtures thereof.
- 20 3. The process according to claim 1 wherein the elastomer is a chloroprene polymer and the organic vulcanizing agent of the adduct is 2-mercaptoimidazoline.
- 25 4. The process according to claim 1 wherein the elastomer is a chloroprene polymer and the organic vulcanizing agents in the adduct are catechol and di-o-tolyl-guanidine.
- 30 5. The process according to any of claims 1-4 wherein said adduct contains from 1 to 35 percent organic vulcanizing agent.
- 35 6. The process according to any of claims 1-5 wherein the lightly calcined magnesia has an iodine adsorption number of from 15 to 220.
- 40 7. A vulcanizable elastomeric composition comprising an unvulcanized rubbery elastomer and an adduct of an organic vulcanizing agent containing up to 20 carbon atoms and a lightly calcined magnesia having an iodine adsorption number of from 10 to 300.
8. The composition according to claim 7 wherein the adduct contains from 1 to 35 percent organic matter.
9. The composition according to claim 7 or 8 wherein the organic vulcanizing agent is selected from amines, aldehyde - amines, guanidines, pyrimidines, thioureas, thiazoles, thiocarbamates, thiuram sulfides, imidazoles, polyhydroxybenzenes or mixtures thereof.
- 50 10. The composition according to any of claims 7-9 wherein the organic vulcanizing agent in said adduct is present in amounts of from 0.05 to 5% by weight of the elastomer.
- 55 11. The composition according to claim 7 wherein the elastomer is unvulcanized chloroprene polymer and said adduct is an adduct of 2-mercaptoimidazoline and said lightly calcined magnesia.
- 60 12. The composition according to claim 7 wherein the elastomer is unvulcanized chloroprene polymer and said adduct is an adduct of catechol and di-o-tolylguanidine and said lightly calcined magnesia.
- 65 13. The process of vulcanizing elastomeric material substantially as herein described with particular reference to the examples.
- 70 14. A vulcanized elastomeric composition substantially as herein described with particular reference to the examples.

STEVENS, LANGER, PARRY
& ROLLINSON
Chartered Patent Agents,
Agents for the Applicants.